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Photoswitchable molecular wires: From a sexithiophene to a dithienylethene and back

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ABSTRACT

Photoswitchable dithienylethene groups, added to both α-ends of a sexithiophene molecular wire, switch reversibly between their open and closed forms upon irradiation. The open form has an excited state lifetime of 500 ps and is highly fluorescent, as is typical for oligothiophenes. In contrast the closed form is non-fluorescent and the excited state lifetime is a shorter by a factor of 100, reminiscent of a dithienylethene. In this system, we control the fundamental character of a molecular system through optical switching; toggling between a sexithiophene molecular wire and a dithienylethene reversibly.

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1. Introduction

In the bottom–up approach to molecular electronics, highly conjugated molecules with multiple functionalities provide important properties, including high charge mobility and the possibility to form rigid structures, together with the possibility to modify materials reversibly after synthesis and even after incorporation into devices. Within the context of functional molecular materials dithienylethenes and oligothiophenes stand out. Photochromic dithienylethene switches are especially interesting because of their often excellent fatigue resistance and the thermal stability in both photochromic states [1,2]. Oligothiophenes form materials that have already proven their versatility in electronic devices such as FETs, OLEDs, photovoltaic cells and molecular wires [3–5]. They provide for high charge mobilities and emission quantum yields, regular morphologies, and show excellent stability. The combination of these two functional units allows for interesting new materials, such as switchable molecular wires.

Recently, we introduced photoswitchable units at both α-ends of a sexithiophene (Fig. 1). These units allow for tuning of the properties of these systems after the compounds are synthesised [6]. In these systems the absorption and fluorescence spectra of the open form exhibit a remarkable dependence on temperature [7]. In the open form the UV/Vis spectrum at 298 K shows a broad unstructured absorption band in solution that becomes increasingly structured below 260 K and is accompanied by a near complete loss in fluorescence intensity. The changes in the absorption spectrum and the dramatic decrease in fluorescence observed with decreasing temperature were ascribed to the formation of aggregates at temperatures below 260 K.

A fundamental challenge facing the design of multifunctional systems arises when the two functional units in a molecular system overlap structurally (Fig. 1); can both units retain their individual characteristics. In the present case, for example, will the sexithiophene unit or the molecular dithienylethene unit dominate the properties of this multi-component system. These questions are of key importance in the development of switchable molecular devices. When two functional components are combined to form a single molecular system, often its properties are determined primarily by only one of the functional units with the second component serving to modify and/or tune these properties. However, it would be highly interesting to design systems in which the fundamental nature of a multi-component system can be changed through reversible switching. Here, steady state and ultrafast time-resolved spectroscopies are employed to explore the behavior of these dithienylethene–sexithiophene multi-component compounds. We show that the fundamental character of the molecule can be toggled between two states: in the open form the molecule behaves as a sexithiophene and in the closed form as a dithienylethene.

2. Experimental

Compound **1oo** (Fig. 1) was available from earlier studies [6]. All chemicals used were of spectroscopic grade or better and were used as received. Steady state experiments were performed in hexane. Absorption spectra were recorded using a HP8453 diode array spectrophotometer or a JASCO V570 dual beam UV/Vis NIR spectrophotometer. Fluorescence spectra were recorded on a JobinYvon

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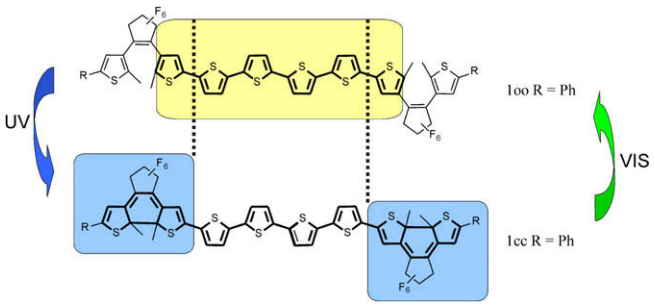

Fig. 1. Molecular structure of compound **1** in the fully open (**1oo**) and fully closed (**1cc**) state. Compound **1** is end-capped with phenyl groups. The suffixes oo and cc indicate that both photochromic units are in the open and closed states, respectively. The dotted lines between the open and closed form indicate the overlap in structure of the sexithiophene and the dithienylethene unit.

Fluorolog Max or a Jasco 7200 fluorimeter. An Oxford instruments Optistat DN was used for temperature dependent measurements.

Details of the transient-absorption acquisition system are described elsewhere [7]. Briefly, for **1oo** the pump pulse was centered at 475 nm (45 fs time resolution, 100 μW). For **1cc** the pump pulse was tuned to 620 nm (33 fs time resolution, 30 μW). Broadband probe pulses (~ 450–750 nm) were generated by focusing part of the output of a Ti:sapphire amplifier into a 1 mm sapphire disk. Build-up of photoproducts was prevented in room temperature measurements by using a 2 mm flow cell with a 30 ml reservoir of the compound dissolved in cyclohexane. Low temperature measurements were recorded at 125 K in isopentane, in a 1 mm cuvette using a cryostat (Optistat CF, Oxford Instruments liq. N_2 cooled cryostat).

Ring-closure of the compound was achieved by irradiation with a UV lamp (Spectroline 312 nm) for approximately 1 min. HPLC analysis showed that full ring closure to the cc state proceeded through the co state [6]. However, isolation of co and cc was precluded by thermal instability with respect to ring opening. Transient spectra show that during the experiments on the closed state the system is in the cc state.

3. Results and discussion

Fig. 2 summarizes the results of steady-state spectroscopy. The absorption spectrum of the sample closed photochemically shows a pronounced bathochromic shift of ~180 nm compared to that of the open form (**1oo**). Such a shift is typical for dithienylethene photochromic switches and is due to changes in the energies of the frontier orbitals [1,8]. The absorption spectrum undergoes a red shift of ~40 nm over a 180 K temperature range (see supporting online information) and is broadened slightly compared with that at room temperature. Even at 120 K, the absorption spectrum does not show structure that would indicate aggregation, in contrast to **1oo**. Furthermore in the open form, the compound is highly fluorescent ($\Phi_{fl} = 0.2$), whereas the closed form is non-fluorescent ($\Phi_{fl} < 10^{-5}$). In summary, the steady state spectra show that the behavior of the closed form does not resemble that of the open form; **1cc** is non-fluorescent and there is no evidence for H-aggregate formation at low temperature.

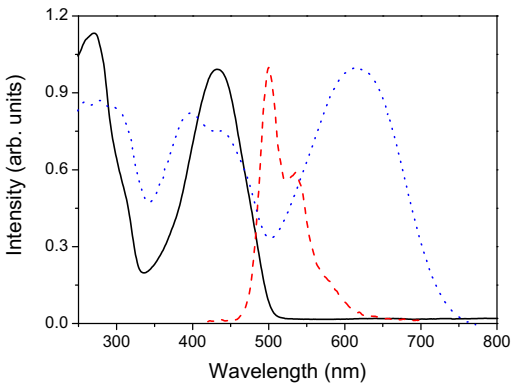

Fig. 2. Absorption spectra of **1oo** (black, solid) and **1cc** (blue, dots) and the fluorescence spectrum of **1oo** (red, dashed). The closed form is non-fluorescent. The individual spectra are normalized to their maxima in the region 430–620 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We now proceed to the analysis of the ultrafast dynamics with particular focus on selective excitation of the closed form. The quantum yield of photochemical ring opening for dithienylethenes is low, typically 1% or less [9]. Therefore, the transient spectra and kinetic traces are virtually free of contributions from the photochromic reaction and the formation of **1oo**. Furthermore, permanent bleaching is not observed in the transient data, allowing for unencumbered analysis of the photophysics of **1cc**. Fig. 3 shows the room temperature transient spectra and decay kinetics of **1cc**. The negative signal (minimum at 614 nm) corresponds in shape to the steady state absorption spectrum. Hence, this signal is assigned to ground state bleach. Between 670 nm and 750 nm, the end of the detection window, a positive signal is observed, that can be assigned to excited state absorption (ESA) from S_1 to S_n. The kinetic traces at 298 K can be fitted globally with a three level sequential model with time constants of 140 fs, 1.6 ps and 6.3 ps. The shapes of the transient spectra of **1cc** at 125 K and 298 K are similar (see Supporting online information Fig. B). The kinetic traces at 125 K are fitted globally with the same model as at room temperature. Time constants resulting from this fit are 90 fs, 1.5 ps and 5.0 ps. Fitting the data at 125 K with the same parameters as the room temperature data resulted in a decrease of the χ^2 of the fit by less than 4%. The errors in the time constants from the global fits are ~10%. Because of the close resemblance in spectral shape of the levels involved in the model, the different time constants cannot be directly linked to a physical process, however, comparison with previous studies is strongly suggestive of certain underlying processes [10–14]. The subpicosecond time constant observed in our data corresponds well with a time constant assigned to the initial decay of the excited state by level crossing (1B–2A) in cyclohexadiene, the core of the dithienylethene molecular switches. From this point onwards the decay proceeds to a minimum on the potential energy surface from which the molecule returns to its electronic ground state. This process is followed by vibrational cooling to allow for relaxation to the minimum of the ground state.

Fig. 3B shows a kinetic trace for **1oo** as a comparison [7]. The closed form (**1cc**) decays by a factor of a hundred times faster than the open form (**1oo**); within the lifetime of **1cc** the signal of the open form is virtually static. Previously we assigned the properties of the **1oo** – the shape and intensity of the fluorescence spectra and the temperature dependent aggregation – to behavior typical of a sexithiophene [7]. However, the properties of the closed state examined here are markedly different from those of sexithiophenes. Instead, the results of both steady state and time resolved spectroscopy are consistent with previous studies of ring closed dithienylethenes [9,15]. Hence, the state – open (**1oo**) or closed (**1cc**) – of the dithienylethene functional units has a profound influence on the nature of this multi-component compound: in the open form it behaves as a sexithiophene and in the closed form as a dithienylethene. This observation is supported by electrochemical measurements reported earlier [6], where it was shown that cyclic voltammetry of **1oo** is typical of end-capped sexithioph-

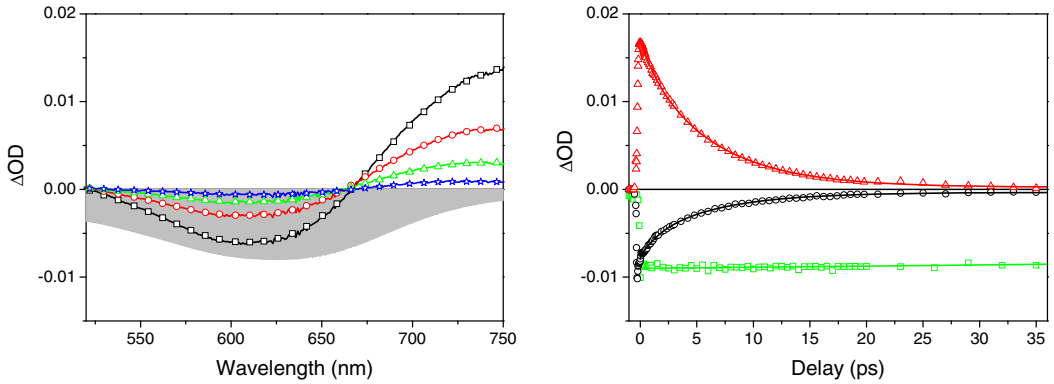

Fig. 3. Transient absorption spectra of the closed form in cyclohexane at 298 K. Pump 620 nm, 33 fs, 30 μW. Panel A shows the spectral evolution of the closed form at 1 ps (black squares), 5 ps (red circles), 10 ps (green triangles), and 20 ps (blue stars). The symbols represent the spectra obtained from global analysis of the data. Panel B shows the temporal evolution of the transient signals at 600 nm (black circles), and 750 nm (red triangles). The steady state absorption spectrum is presented scaled and in grey shading. As a comparison panel B shows the time evolution of the open form at 545 nm (green squares). The solid lines are global fits of the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

enes. However, upon ring closing to **1cc**, the reduction potential observed is characteristic of dithienylethenes in the closed form. The shift in reduction potential corresponds closely to the shift of the lowest absorption in the UV/Vis absorption spectrum.

4. Conclusion

The behavior of this molecular wire can be changed reversibly between that of a sexithiophene with photochromic end groups and that of an oligothiophene bridged bis-dithienylethene. This change is manifested by a dramatic difference in fluorescence intensity and excited state lifetime between **1oo** and **1cc**. Thus, by adding dithienylethene photochromic groups to the α-ends of a sexithiophene a simple stimulus, light, can be used for post-synthetic tuning of the molecule. In the open state the electronic and excited state properties are essentially those of an oligothiophene molecular wire perturbed by the thienylethene end groups. In the closed state the molecule shows photochemical behavior that is essentially that of a dithienylethene molecule substituted with thiophene units. This ability to toggle the primary functionality of a multi-component molecular system opens interesting prospects for the development of bifunctional molecular electronic systems, not least in the fundamental concept of switching of molecular conductance.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.08.013.

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